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(54) SURFACE-ACTIVE CONDENSATION PRODUCTS OF DIETHANOLAMINE AND CARBOXYLIC ACIDS

- (71) We, WITCO CHEMICAL COMPANY, INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, of 277 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to surface-active condensation products of diethanolamine and carboxylic acids and, more particularly, to surfactant compositions comprising them.
- Condensation products of diethanolamine with long chain monocarboxylic acids, and condensation products of diethanolamine with aromatic polycarboxylic acids have long been known in the art, the former being disclosed, for instance, in U.S. Patent Specifications Nos. 21,530 and 2,089,212, and the latter in U.S. Patent Specification No. 2,094,608. The condensation products disclosed in U.S. Patent Specification No. 2,089,212, exemplified particularly by condensation products having 2 moles of diethanolamine and approximately 1 mole of C_{12} — C_{14} fatty acids, have gone into large commercial use as detergents and for other surfactant uses in a number of industries.
- The prior art products of the type exemplified by condensation products of diethanolamine and C_{12} — C_{14} fatty acids, particularly those in which the mole ratio of the diethanolamine to the C_{12} — C_{14} fatty acids is approximately 2 to 1, are very predominately amides, with quite small amounts of esters and esteramides and containing, also, uncondensed diethanolamine, at least some of which is present in the final condensation product in the form of diethanolamine soaps
- of the C_{12} — C_{14} fatty acids. Such condensation products are quite readily dispersible in water. Generally speaking, they have reasonable solubility in water, the extent of such water-solubility being related to the extent to which amidification of the diethanolamine with the C_{12} — C_{14} acids has been effected. It is known to the art that, if the condensation reaction is carried out so that there is a relatively high content of esters or ester-amides in the final condensation product, water-solubility is decreased. Hence, techniques have heretofore been developed to influence equilibrium conditions so as to influence the condensation reaction, or resort has been had to post-condensation reaction treatments, to bring about amide formation to the maximum extent reasonably possible. Condensation products of the type referred to above, in which approximately 2 moles of diethanolamine are condensed with 1 mole of C_{12} — C_{14} fatty acids, are generally characterized by a pH, say in a 3% aqueous solution, of about 9.2.
- According to the present invention, there is provided a process for producing a water-soluble surfactant which process comprises heating a mixture to cause condensation of the constituents thereof, the mixture comprising (i) an aliphatic monocarboxylic acid, or an ester or anhydride thereof, said monocarboxylic acid having 8 to 24 carbon atoms, (ii) 1.6 to 3.6 moles per mole of aliphatic carboxylic acid, ester or anhydride, of an aromatic di-, tri-, tetra-, or hexa- carboxylic acid, or ester or anhydride thereof, the foresaid aromatic carboxylic acid, ester or anhydride optionally having ring substitution provided that any substituent does not have an adverse effect on the water-solubility of the resulting condensation products, the amounts of the aforesaid acids, anhydrides and esters and the amounts of the substituted acid being on a free acid basis, and (iii)

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(1.2+x+y) moles of diethanolamine per mole of aliphatic carboxylic acid, ester or anhydride on a free acid basis, where x has a value of 2.4 for each mole of aromatic dicarboxylic acid, 3.6 for each mole of aromatic tricarboxylic acid, 4.8 for each mole of aromatic tetracarboxylic acid and 7.2 for each mole of aromatic hexacarboxylic acid, and where y has a value of from 0 to 20 moles. Preferably the mixture comprises not more than 1.5 moles of additional diethanolamine given by y. Generally the heating of the mixture is carried out at a temperature of 180°F. to 400°F. and preferably at a temperature of 300°F. to 350°F. Advantageously, the mixture is heated under conditions of agitation.

The aliphatic monocarboxylic acid is advantageously a source of fatty acid containing predominantly C₁₂-C₁₄ aliphatic monocarboxylic acids. Examples of long-chain monocarboxylic acids include caprylic acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, tall oil fatty acids, stearic acid, and tallow fatty acids, and mixtures thereof. As mentioned hereinbefore, the aliphatic acid may be in the form of an ester of the free acid and examples of such include methyl esters and glyceride esters such as triglyceride esters. It should be noted that in the condensation reactions elimination of, for instance, methyl alcohol in the case of methyl esters, occurs. Methyl alcohol will evaporate while, in the case of the glycerol moiety of glyceride esters, the glycerol which breaks off forms an inert constituent of the reaction products. No disadvantage has, however, been due to this.

Generally the aliphatic carboxylic acids, when derived from animal or vegetable sources, contains 8 to 18 carbon atoms. As mentioned above, it is advantageous to employ commercial sources of fatty acids containing predominantly from 2 to 14 carbons. This is particularly advantageous where the intended use of the condensation products is for detergent purposes.

From an economic standpoint, commercial mixtures of fatty acids, such as those specifically exemplified hereinbefore, are employed. For instance, coconut oil fatty acids or special fractions thereof which are especially high in lauric acid or myristic acid, or mixtures of the C₁₂ and C₁₄ fatty acids mentioned already can be used. Where, as stated above, the long-chain monocarboxylic acid is supplied in the form of an ester, the ester may be methyl ester of lauric acid, methyl ester of myristic acid, methyl ester of coconut oil mixed fatty acids.

The aromatic carboxylic acid, which may be in the form of an ester, such as the methyl or ethyl ester, anhydride or substitution derivative as mentioned hereinbefore, may particularly be mononuclear polycarboxylic

acids or anhydrides illustrative examples of which are phthalic acid, advantageously as phthalic anhydride; isophthalic acid; hexahydrophthalic acid; terephthalic acid; mellitic acid, advantageously as mellitic anhydride; prehnitic acid; mellophanic acid; pyromellitic acid; hemimellitic acid; trimellitic acid; trimesic acid and diphenic anhydride; and aromatic polycarboxylic acids having ring substituents of a type which do not adversely affect the water-solubility of the condensation products, suitable substituents being, for instance, hydroxyl and sulfonate groups. Phthalic anhydride is especially useful in the production of the condensation products of this invention and its use therefore is particularly preferred. It will obviously be appreciated that mixtures of two or more of the aromatic carboxylic acids may be used.

When the aromatic carboxylic acid is dicarboxylic, the acid may be present in, for example, an amount of 2 moles per mole of aliphatic carboxylic acid, the diethanolamine being present in an amount of 6 to 7 moles, preferably 6.5 to 6.7 moles. According to an alternative embodiment there is provided a process, as broadly described herein, in which the aromatic acid is a tricarboxylic acid present in the mixture in an amount of 2 moles per mole of the aliphatic carboxylic acid, the mixture also containing 8.5 to 8.7 moles of diethanolamine. In another form of this embodiment the amount of tricarboxylic acid, per mole of aliphatic monocarboxylic acid, is 3 moles per mole of the aliphatic carboxylic acid and the diethanolamine is present in an amount of 12.0 to 12.5 moles.

According to a specific embodiment of the invention the aliphatic carboxylic acid is a fatty acid containing from 12 to 18 carbon atoms, the aromatic carboxylic acid is a mononuclear aromatic dicarboxylic acid in an amount of 2 molar parts per mole of the aliphatic carboxylic acid, and the diethanolamine is in an amount of 6 to 7.5 molar parts, the mixture being heated at a temperature in the range of 180°F. to 400°F. until the resulting condensation product solubility is such that when one drop thereof is added to 50 cc. of tap water as well as to 50 cc. each of 25% aqueous solutions of caustic soda, sulfuric acid, and sodium chloride, a clear solution is produced.

The condensation reaction, to split out water or an alcohol, as the case may be, depending upon whether the free long-chain monocarboxylic acid or an ester thereof is used, is carried out, generally speaking, at a temperature in the range of 180°F. to 400°F., preferably 300°F. to 350°F., as mentioned hereinbefore, with reaction times of 1½ hours to 6 hours, usually 2 hours to 4 hours. The condensation reaction is carried out under atmospheric pressure or in vacuo or in the presence of an inert gas, such as nitrogen or

argon, and desirably under conditions of agitation of the reaction mixture. While condensation catalysts, particularly alkalis or alkaline materials such as caustic soda or caustic potash or sodium methylate, can be used, they are unnecessary to the production of the condensation products of the present invention. Where catalysts are used, and the long-chain monocarboxylic acids are utilized in the form of their methyl esters, the condensation reactions can be carried out in the lower temperature ranges without unduly long reaction times.

The condensation products which represent the most important embodiments of the present invention are characterized by the solubility characteristics recited hereafter in Example 1, namely, one drop of the condensation product, when added to 50 ml of separate aqueous solutions of (1) 25% caustic soda, (2) 25% sulfuric acid, and (3) 25% brine, and (4) 50 ml of tap water, will, in each case, produce a clear solution.

Especially important condensation products of this invention are those produced by reacting (a) 1 mol of lauric acid, or myristic acid, or coconut oil mixed fatty acids or fractions thereof which are particularly high in their content of C_{12} — C_{14} fatty acids, as such, or in the form of an ester such as the methyl esters or the triglyceride esters of said fatty acids (taking into account the fatty acids content thereof), (b) 2 molar parts of phthalic anhydride, and (c) from about 6 to 6.8 and, preferably from 6.5 to 6.6 molar parts of diethanolamine; the reaction being carried out at a temperature in the range of about 300°F. to 335°F. and, better still, in the range of about 320°F. to 330°F., under a vacuum, generally of the order of 20 to 27 inches Hg. and, preferably, in the range of about 24 to 26 inches Hg., for about 2 to 4 hours or until the solubility characteristics referred to above are obtained, whereupon the condensation products are promptly cooled so as rapidly to reduce the temperature thereof to about 210°F., or less if desired. Thereafter water is admixed therewith, generally in proportions of 10% to 15%, by weight of the condensation products, so as to render the resulting composition pourable and pumpable.

Diethanolamine, in its commercial form as purchased, is most advantageously used as such in the production of the condensation products of this invention. Relatively small or minor proportions of other alkanolamines can be added thereto or admixed therewith and the condensation products of this invention produced therefrom. Such other alkanolamines include, for example, monoethanolamine, mono - isopropanolamine, diisopropanolamine, diethylethanolamine, and glycerolamines. Where utilized, they should not, generally speaking, be employed in

amounts in excess of about 10% of the weight of the diethanolamine.

The present invention will now be described by way of example:

EXAMPLE 1:

(a) A stainless steel kettle is charged with 2784 pounds of diethanolamine, the contents are heated to about 215°F., agitated and a stream of gaseous nitrogen is bubbled through the diethanolamine. Then, 816 pounds of coconut oil mixed fatty acids are added while maintaining the temperature in the range of 210°F. to 220°F., followed by the addition of 1200 pounds of phthalic anhydride, all under conditions of agitation. The kettle is closed, then placed under a vacuum of 24 to 26 inches of mercury and the contents heated to 330°F and held under said vacuum and temperature conditions for 2 hours or until a sample, when added to separate aqueous solutions of (a) 25% caustic soda, (2) 25% sulfuric acid, and (3) 25% brine, and (4) plain tap water, in the form of one drop of the condensation product to 50 ml of each of said solutions and of the tap water, produces a clear solution. Before sampling, the vacuum is desirably reduced to 8 inches with nitrogen gas.

(b) The condensation product, weighing 4464 pounds, is rapidly passed through a heat exchanger, to cool it quickly to about 212°F, into a holding tank, the vacuum and nitrogen are cut, and 400 pounds of water are sucked into said holding tank, under conditions of agitation, until the final solution is homogeneous. The water content can be adjusted as desired, preferably to about 10 or 12%, by weight, of the finished solution. The condensation product, prior to admixture of the water therewith, is a clear, amber glassy gel essentially non-flowing at room temperature, becoming fluid at about 175°F. It can also be rendered fluid, as indicated above, by the addition thereto of suitable amounts of water, or by the addition of suitable amounts of ethanol.

EXAMPLE 2:

200 pounds of coconut oil mixed fatty acids, 332 pounds of isophthalic acid, and 695 pounds of diethanolamine are placed in a kettle and heated at about 300°F for 4 hours under a vacuum of about 26 inches of mercury, with agitation, or until the solubility characteristics specified in Example 1 are obtained. The resulting condensation product is then rapidly cooled to room temperature.

EXAMPLE 3:

282 pounds of stearic acid, 444 pounds of phthalic anhydride, and 950 pounds of diethanolamine are placed in a kettle and heated at about 300°F for 4 hours under a

blanket of gaseous nitrogen, with agitation. The resulting condensation product is rapidly cooled to room temperature.

EXAMPLE 4:

213 pounds of the methyl esters of coconut oil mixed fatty acids, 398 pounds of dimethyl phthalate, 685 pounds of diethanolamine, and 10 pounds of sodium methylate are placed in a kettle and heated at about 275°F for 4 hours under a vacuum of about 26 inches of mercury, with agitation, or until the solubility characteristics specified in Example 1 are obtained. The resulting condensation product is rapidly cooled to room temperature.

EXAMPLE 5:

200 pounds of a fraction of coconut mixed fatty acids containing at least 90% lauric acid, 296 pounds of phthalic anhydride, and 700 pounds of diethanolamine are placed in a kettle and heated at about 330°F for 2 hours under a vacuum of about 26 inches of mercury, with agitation, or until the solubility characteristics set forth in Example 1 are obtained. The resulting condensation product is rapidly cooled to room temperature.

In addition to possessing excellent water-solubility, and excellent solubility in aqueous alkaline and acidic solutions as well as in aqueous solutions of various electrolytes, the condensation products made pursuant to this invention are, generally, readily soluble in various alcohols, ketones, chlorinated hydrocarbons and aromatic hydrocarbons such as methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, trichloroethylene, benzene and toluene. They exhibit surface activity over a wide range of concentrations in water and in aqueous solutions of acids, alkalis, and various salts, from very dilute to very concentrated. Illustrative of such solutions in which said condensation products exhibit foaming and other surface active properties are 25% solutions in water of potassium hydroxide, sodium hydroxide, sulfuric acid, and sodium chloride. In the case of the sodium hydroxide solution, the condensation products have a gelling effect thereon which creates an apparent haze in said solution due to air entrained in the gel.

In the case of the condensation product of Example 1, surface tension measurements, using a concentration of 0.5%, by weight, in distilled water and in the stated solutions show the following results:

Sample	Surface Tension (dynes/cm)
Distilled water	28.8
25% aqueous solution of NaOH	33.2
25% aqueous solution of H ₂ SO ₄	31.3
25% aqueous solution of NaCl	38.1

It may be noted that most synthetic detergents lower the surface tension of water generally to somewhere in the approximate range of 30 to 35 dynes/cm when present in concentrations from 0.1 to 0.5% but are ineffective in strong or concentrated solutions of electrolytes. Condensation products of the present invention, exemplified by Example 1, however, are effective not only in water but also in a wide range of concentrations of electrolytes in aqueous solution.

Another highly desirable property of condensation products made in accordance with the present invention is that they do not effect appreciable increase in viscosity in water solutions as do many commercial synthetic detergents. Thus, by way of illustration the effect upon viscosity of water was measured by the addition thereto of the condensation product of Example 1, over a range up to 8%, and compared with a like range of concentrations of (1) dodecyl benzene sodium sulfonate and (2) a commercial 9 mol ethylene oxide adduct of nonylphenol. In concentrations up to 5%, the viscosity of the water solutions of each of the three products tested remained relatively low (although the viscosity of the solutions of the condensation product of the present invention was generally distinctly lower); but, in the range of concentrations from about 5 to 8%, there was a very sharp increase in the viscosities of the solutions of the dodecyl benzene sodium sulfonate and the aforesaid adduct of nonylphenol whereas the increase in the viscosity of the solutions of the condensation product of this invention was very slight.

Condensation products of this invention, typified by Example 1, exhibit a lower viscosity in water solution than do alkali metal soaps, various detergent type ethylene oxide adducts, and alkyl benzene sulfonates such as dodecyl benzene sodium sulfonate. The addition of said condensation products to aqueous solutions of said soaps or of said detergents does not reduce the viscosity thereof. The aforesaid condensation products have a hydrotropic effect upon various detergents both in fresh water and in water solutions of various electrolytes, that is, when said condensation products are added in sufficient quantities, they solubilize the detergents in aqueous solutions of electrolytes in which said detergents are not ordinarily soluble. By way of illustration, a commercial nonylphenoxy poly (ethyleneoxy) ethanol forms a cloudy dispersion in a 20% solution of sodium chloride in water. When 0.1 g of the condensation product of Example 1 for each 0.5 g of nonylphenoxy poly (ethyleneoxy) ethanol is added to said water solution of sodium chloride, the solution becomes completely clear. It may also be noted that, while lauric diethanolamides are generally good

foaming agents and foam stabilizers, the condensation products of this invention are generally low, quick-breaking foamers.

As previously noted, another aspect of the present invention is based upon the discovery that a surprising and highly desirable enhancement in the solubility and stability of the above described condensation products of the present invention in strong alkaline solutions is obtained by incorporating therewith a sulfonated aliphatic unsaturated carboxylic acid or water-soluble salts thereof. The resulting improved surfactant compositions comprise, by weight, for instance and by way of illustration, about 50 to 95 percent of the previously described condensation products of diethanolamine, long chain monocarboxylic acids containing from 8 to 14 carbon atoms and aromatic polycarboxylic acids, made as described above, and about 50 to 5 percent and preferably between about 10 and 25 percent of a sulfonated aliphatic unsaturated carboxylic acids or the alkali metal, ammonium or amine salts of said sulfonated aliphatic unsaturated carboxylic acids or mixtures of the same.

The sulfonated aliphatic unsaturated carboxylic acids used pursuant to this aspect of the present invention contain from 4 to 22 carbon atoms, especially 16 to 18 carbon atoms and can be prepared by any of the well known sulfonation procedures including reacting an unsaturated aliphatic carboxylic acid with sodium bisulfite, sulfur trioxide, oleum, chlorosulfonic acid, sodium sulfite or sulfuric acid. The unsaturated aliphatic carboxylic acids which are suitable for preparing the sulfonated acids may be supplied in various forms as, for instance, the free acid or as an anhydride of a dibasic acid as, for example, maleic anhydride. Illustrative examples of the unsaturated aliphatic carboxylic acids include oleic acid, linoleic acid, linolenic acid, and tall oil fatty acids.

The following examples are illustrative of the practice of that aspect of the present invention pursuant to which sulfonated aliphatic unsaturated carboxylic acids or the water-soluble salts thereof are admixed with the condensation products. Again, these examples are not to be construed as in any way limitative of the scope of this aspect of the present invention since numerous other surfactant compositions can readily be produced in the light of the teachings and guiding principles disclosed herein.

EXAMPLE 6:

To 80 weight parts of the condensation product of Example 1 were added 20 weight parts of the sodium salt of sulfonated oleic acid. Several drops of the resulting solution were then added to tap water and to a 25 percent aqueous solution of sodium metasilicate in the ratio of one drop of sample

to 50 ml of solution. In both instances, a clear, stable solution was formed. In contrast thereto, when the condensation product of Example 1 was added to a 25 percent aqueous solution of sodium metasilicate, a hazy product resulted which settled on standing.

EXAMPLE 7:

To 70 weight parts of the condensation product of Example 2 were added 30 weight parts of sulfonated tall oil fatty acids. Several drops of this composition were added to tap water and to a 25 percent aqueous solution of sodium metasilicate in the same ratio as above with clear stable solutions being formed in both instances. Again, in contrast thereto, the addition of several drops of the condensation product of Example 2 to a 25 percent aqueous solution of sodium metasilicate in the ratio of one drop per 50 ml of solution resulted in a hazy product that settled on standing.

EXAMPLE 8:

40 weight parts of the sodium salt of sulfonated maleic anhydride were blended with 60 weight parts of the condensation product of Example 4. The solubility tests described above in Example 6 were run with this composition and clear stable solutions were obtained. A sample of the condensation product of Example 4 when added to a 25 percent aqueous sodium metasilicate solution again resulted in a hazy product which settled out on standing.

EXAMPLE 9:

A blend of 40 percent by weight of sulfonated linseed oil fatty acids and 60 percent by weight of the condensation product of Example 5 was prepared and evaluated as in Examples 6, 7 and 8 with similar results being obtained.

Surfactant compositions made as described in illustrative Examples 6, 7, 8 and 9 of the present invention are clear liquid solutions that are characterized by exceptional solubility in water as well as in aqueous alkaline solutions and in aqueous solutions of various electrolytes. Furthermore, the pH of such surfactant compositions is generally materially lower than the pH of prior art products referred to previously, the pH, for instance, in 3% solutions in water, falling within the approximate range of 7.4 to 7.7. In addition to possessing excellent water-solubility, and excellent solubility in aqueous alkaline solutions as well as in aqueous solutions of various electrolytes, such surfactant compositions are, generally, readily soluble in various alcohols, ketones, chlorinated hydrocarbons and aromatic hydrocarbons such as methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, trichlorethylene, benzene

and toluene. They exhibit surface activity over a wide range of concentrations in water and in aqueous solutions of alkalis, and various salts, from very dilute to very concentrated. Illustrative of such solutions in which said surfactant compositions exhibit foaming and other surface active properties are 30% solutions in water of potassium hydroxide, sodium hydroxide, and sodium chloride. In the case of the sodium hydroxide solution, the condensation products of Examples 1 to 5 have a gelling effect thereon which creates an apparent haze in said solution due to air entrained in the gel.

In the case of the surfactant composition of Example 6, surface tension measurements, using various concentrations by weight, in distilled water and in the stated solution of mixed electrolyte show the following results:

20	Distilled water (Conc. by wt.)	Surface tension (dynes/cm.)
	.01% surfactant	33.2
	0.1% surfactant	31.8
	0.5% surfactant	32.7
25	11% Sulfuric Acid, 1% Copper Sulfate Solution (Conc. by wt.)	Surface tension dynes/cm.)
	.01% surfactant	32.1
	0.1% surfactant	32.3
30	0.5% surfactant	31.9

It may be noted that most synthetic detergents lower the surface tension of water generally to somewhere in the approximate range of 30 to 35 dynes/cm when present in concentrations from 0.1 to 0.5% but are ineffective in strong or concentrated solutions of electrolytes. Surfactant compositions exemplified by Example 6, however, are effective not only in water but also in a wide range of concentrations of electrolytes in aqueous solution.

Various supplemental ingredients can be incorporated into the surfactant composition of the present invention or used in conjunction therewith to meet certain specific end uses. By way of example, liquid alkaline materials may be added to the compositions of Examples 6 to 9 to increase the pH of the surfactant composition, act as a coupling agent for the sulfonated acid and condensation product or serve as a diluent for the surfactant composition. Illustrative examples of liquid alkaline materials include alkanolamines, polyamines, ammonia or aqueous solutions of water-soluble bases such as sodium or potassium hydroxide or carbonate.

The condensation products and the surfactant compositions of the present invention have utility in a wide variety of fields. Apart from their use as detergents, they are effective as emulsifiers, where, for instance, they

produce aqueous-oleaginous emulsions which are useful in many fields such as cleaning and degreasing of metals, cosmetic creams, shampoos, and pesticidal compositions. One illustrative utility as an emulsifying agent is the preparation of emulsions of water with hydrophobic organic solvents such as toluene and xylene. Good emulsions can be made, for example, of (1) water, (2) 25% aqueous solution of sodium hydroxide, (3) 25% aqueous solution of potassium hydroxide, (4) 25% aqueous solution of sulfuric acid, and (5) aqueous solution of sodium chloride, in each case with 10% toluene, using 1% of a condensation product such as is produced in accordance with Example 1 or a surfactant composition such as is produced in accordance with Example 6.

The condensation products and the surfactant compositions of the invention find use in the textile industry in kier boiling, wool fulling, cotton mercerizing, dyeing and soaping off operations; in the petroleum industry as water flood additives, oil field emulsions demulsifiers, drilling mud additives, in work over fluids and in acidizing operations; in the steel industry as pickling bath additives, plating bath additives, wetting agents for caustic solutions, in lubricant compositions, and as corrosion inhibitors; in the detergent, cleansing and cosmetic fields, as in built liquid detergents, in specialized industrial cleaning compositions, synthetic detergent bars, specialty shampoos and specialty cleaners; in the paper industry, as wetting agents in pulp digestion operations and as gelling agents in sizing operations; and, in general, for uses in which detergents and surfactants are commonly employed in the arts.

It will be appreciated from the foregoing specific description that condensation products made according to the process of the invention are very soluble in water as well as in aqueous alkaline and acidic solutions and in aqueous solutions of various electrolytes. This is despite the fact that the reactants and the molar ratios thereof which are utilized would seem to indicate that products of impaired water-solubility would be obtained. Furthermore, the pH of the condensation products is generally lower than the pH of the condensation products of prior art processes, the pH of typical condensation products of the present invention, for instance, in 3% solutions in water, fall within the range of 7.4 to 7.7. The condensation products of this invention appear to have an appreciable content of residual uncondensed carboxyl groups which are believed to be present in the form of the monoamide of the aromatic polybasic acid, the monoamide being present in the form of the diethanolamine salt. This may account for the low pH values. Despite these residual un-

condensed carboxyl groups, which, in diethanolamine-higher fatty acid condensation products of prior art processes, also tend to impair water-solubility, the condensation products of the present invention, as stated above, possess, surprisingly, exceptionally good water-solubility, especially in the presence of electrolytes.

WHAT WE CLAIM IS:—

1. A process for producing a water-soluble surfactant which process comprises heating a mixture to cause condensation of the constituents thereof, the mixture comprising (i) an aliphatic monocarboxylic acid, or an ester or anhydride thereof, said monocarboxylic acid having 8 to 24 carbon atoms, (ii) 1.6 to 3.6 moles, per mole of aliphatic carboxylic acid, ester or anhydride, of an aromatic di-, tri-, tetra-, or hexa- carboxylic acid, or ester or anhydride thereof, the aforesaid aromatic carboxylic acid, ester or anhydride optionally having ring substitution provided that any substituent does not have an adverse effect on the water-solubility of the resulting condensation products, the amounts of the aforesaid acids, anhydrides and esters and the amounts of the substituted acid being on a free acid basis and (iii) $(1.2+x+y)$ moles of diethanolamine, per mole of aliphatic carboxylic acid, ester or anhydride on a free acid basis, where x has a value of 2.4 for each mole of aromatic dicarboxylic acid, 3.6 for each mole of aromatic tricarboxylic acid, 4.8 for each mole of aromatic tetracarboxylic acid and 7.2 for each mole of aromatic hexacarboxylic acid, and where y has a value of from 0 to 20 moles.

2. A process as claimed in claim 1, wherein the temperature at which the mixture is heated is 300°F. to 350°F.

3. A process as claimed in claim 1 or claim 2, wherein the mixture is heated under conditions of agitation.

4. A process as claimed in any one of claims 1 to 3, wherein said aliphatic monocarboxylic acid is a source of fatty acid containing predominantly C_{12} — C_{14} aliphatic monocarboxylic acid.

5. A process as claimed in any one of claims 1 to 3, wherein said aliphatic monocarboxylic acid is caprylic acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, tall oil fatty acids, stearic acid, and tallow fatty acids, or a mixture thereof.

6. A process as claimed in any preceding claim, wherein said mixture comprises not more than 1.5 moles of additional diethanolamine given by y .

7. A process as claimed in any preceding claim, wherein said aromatic carboxylic acid is a dicarboxylic acid and is present in an amount of 2 moles per mole of the said ali-

phatic carboxylic acid, and the amount of diethanolamine is 6 to 7 moles.

8. A process as claimed in claim 7, wherein the amount of diethanolamine is 6.5 to 6.7 moles.

9. A process as claimed in any one of claims 1 to 6, wherein said aromatic carboxylic acid is a tricarboxylic acid and is present in an amount of 2 moles per mole of the said aliphatic carboxylic acid, and the amount of diethanolamine is 8.5 to 8.7 moles.

10. A process as claimed in any one of claims 1 to 6, wherein said aromatic carboxylic acid is a tricarboxylic acid and is present in an amount of 3 moles per mole of the said aliphatic carboxylic acid, and the amount of diethanolamine is 12 to 12.5 moles.

11. A process as claimed in any preceding claim, wherein said aromatic carboxylic acid is isophthalic acid; hexhydrophthalic acid; terephthalic acid; mellitic acid, prehnitic acid; mellophanic acid; pyromellitic acid; hemimellitic acid; trimellitic acid; trimesic acid or a mixture thereof.

12. A process as claimed in any of claims 1 to 10, wherein the aromatic carboxylic anhydride is phthalic anhydride.

13. A process as claimed in any one of claims 1 to 10, wherein the aromatic carboxylic anhydride is diphenic anhydride or mellitic anhydride.

14. A process as claimed in claim 1, in which the aliphatic carboxylic acid is a fatty acid containing from 12 to 18 carbon atoms, the aromatic carboxylic acid is a mononuclear aromatic dicarboxylic acid in an amount of 2 molar parts per mole of the said aliphatic carboxylate acid, and the diethanolamine is in an amount of 6 to 7.5 molar parts, the mixture being heated at a temperature in the range of 180°F. to 400°F. until the resulting condensation product solubility is such that, when one drop thereof is added to 50 cc of tap water as well as to 50 cc each of 25% aqueous solutions of caustic soda, sulfuric acid and sodium chloride, a clear solution is produced.

15. A process as claimed in claim 1, in which the aliphatic carboxylic acid is a fatty acid containing predominantly C_{12} — C_{14} fatty acids, the aromatic carboxylic anhydride is phthalic anhydride, in an amount of 2 molar parts per mole of the said aliphatic carboxylic acid, and the diethanolamine is in an amount of 6 to 6.8 molar parts, the mixture being heated under a vacuum of 20 to 27 inches of mercury at a temperature in the range of about 300°F. to 335°F. for about 2 to 4 hours, and then rapidly cooled to about 210°F.

16. A process as claimed in claim 15, wherein said temperature is 320°F. to 330°F.

17. A process as claimed in claim 15 or

claim 16, wherein said vacuum is 24 to 26 inches of mercury.

5 18. A process as claimed in claim 1 and substantially as hereinbefore specifically described.

19. A water-soluble surfactant whenever prepared by a process as claimed in any preceding claim.

10 20. A surfactant composition comprising a surfactant as claimed in claim 19 and one or more sulfonated aliphatic unsaturated carboxylic acids or alkali metal, ammonium or amino salts thereof, said carboxylic acid having 4 to 22 carbon atoms.

15 21. A composition as claimed in claim 20, wherein said carboxylic acids contain 16 to 18 carbon atoms.

22. A composition as claimed in claim 20

or claim 21, wherein the amount of said surfactant is 50% to 95% by weight and the amount of sulfonated carboxylic acid or a salt thereof as aforesaid is 5% to 50% by weight. 20

23. A composition as claimed in claim 22, wherein the said sulfonated carboxylic acid or salt is in an amount of 10% to 25% by weight. 25

24. A composition as claimed in claim 20 and substantially as hereinbefore specifically described. 30

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